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(54) Title: CLEANING GELS

(57) Abstract

The invention relates to a cleaner concentrate composition which can be diluted to form a viscous use solution, the cleaner composition comprising: an ammonium compound and/or an amphoteric compound and an anionic surfactant, wherein the composition is free of amine oxide.

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#### CLEANING GELS

### Field of the invention

The present invention concerns cleaning compositions, and more specifically cleaning compositions which can be diluted in order to provide cleaning gels.

## Background of the invention

For the cleaning of hard surfaces and objects, particularly in industrial, institutional and catering environments,

10 cleaning products in the form of gels, which have a prolonged contact with the target surface to be cleaned, are known.

A problem with known gels is that they comprise amine oxide as a gelling agent, which is environmentally harmful, for example by forming nitrosoamines.

An object of the present invention is to yield a gel cleaner, free of amine oxide.

The inventors have surprisingly found that said object can be achieved by applying an ammonium compound, preferably a quaternay or a ternary ammonium compound instead of amine oxide as a gelling agent, and that said ammonium compound can be used to yield an effective cleaning gel.

## Definition of the invention

- According to a first aspect of the present invention, there is provided a cleaner concentrate composition which can be diluted to form a viscous use solution, the cleaner composition comprising:
- an ammonium compound and/or an amphoteric compound; and
  30 an anionic surfactant, wherein the composition is free of amine oxide.

Since this cleaner composition is free of amine oxide, environmentally harmful effects are reduced.

A second aspect of the present invention provides a cleaning method comprising the steps of diluting a

concentrate composition according to the invention with water to a concentration to yield a desired viscosity and applying the composition thus diluted to a target surface. Further aspects of the present invention provide a cleaning gel obtainable by diluting with water the concentrate composition of the invention, and the use of said cleaning gel for cleaning target surfaces.

## Detailed description of the invention

10 When in use for cleaning a surface, the cleaner concentrate composition of the present invention is desirably diluted with water to a concentration of from 1 to 20%, preferably from 2 to 10%, by weight, so as to yield a cleaning gel having a suitable viscosity. Particularly when cleaning verticle surfaces, said cleaning gel should have sufficient viscosity for obtaining effective cleaning performance.

The ammonium compound present in the composition of the invention is effectively a quaternary or a ternary ammonium compound. More preferably, said ammonium compound is selected from the group consisting essentially of benzalkonium chloride and primary, secondary or tertiary amines (C12-C27).

If a quaternary ammonium compound is used, it has desirably a chain length of C8-C20, preferably C12-C16.

A tertiary amine is effectively present for obtaining viscous use solution having a pH-value of 9.5-10, whereas a secondary amine is suitably used when a viscous use solution having a pH of 3.5-4.0 is needed.

- The ammonium compound is preferably present at a concentration of from 1 to 25%, more preferably from 1 to 10%, by weight of the concentrate composition of the invention.
- 35 Preferably, the anionic surfactant present in the concentrate composition of the invention consists one or

more fatty acids neutralised by an alkaline source, preferably an alkaline metal salt such as a sodium salt, these forming a soap. Effectively, said anionic surfactant includes saturated and unsaturated fatty acids in a weight ratio of 1:5, preferably 1:2. Preferably, the fatty acids are selected from the group consisting essentially of oleic acid, palmitic acid, caprylic acid and isostearic acid. The alkaline source is preferably present in the concentrate composition of the invention at a concentration of 5 to 40% by eight.

Desirably, the concentrate composition of the present invention further comprises a cleaning agent selected from the group consisting of a secondary alkane sulphonate, an alkane sulphate, an ether sulphate, and mixtures thereof. More preferably, the concentrate composition of the invention includes a secondary alkane sulphonate at a concentration of from 1 to 25% by weight.

In order to boost the cleaning performance thereof, the concentrate composition of the invention may effectively further comprise a nonionic surfactant.

A suitable further component of the concentrate composition of the invention is a solvent, which can be effectively used for establishing the desired viscosity of the use solution to be obtained from said concentrate by dilution. Said solvent is preferably selected from the group consisting of isopropanol, ethanol, hexylene glycol, propylene glycol, diethylene glycol, monoethyl/butyl ether, dioxitol butyl dioxitol, and mixtures thereof.

A further preferred component of the concentrate composition of the invention is a sequestrant, said sequestrant being desirably present therein at a level of 0.1 to 15% by weight. Said sequestrant is preferably selected from the group consisting of ethylene-diamine-

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tetraacetic acid, nitrilo-tri-acetic acid, citric acid, methyl-glycine-diacetic acid, serine diacetic acid, alkaline salts thereof, and mixtures thereof.

5 The concentrate composition of the invention may effectively further include threshold agents such as phosphonates, polyacrylates and hydrotropes, and/or iron binders such as sodium gluconate. These threshold agents and iron binders may be suitably present at a concentration of from 0.1 to 5% by weight.

The concentrate composition preferably has a flash point of between 25-50°C.

The present invention will now be illustrated by way of the following examples.

Field trials have been carried out with the following embodiments of a composition according to the present invention.

Figures 1-3 show the measured ratio of saturated to unsaturated fatty acids of compositions 1 to 3 respectively.

Composition 1: General purpose liquid detergent for foamgel and gel cleaning (low flash point).

	Raw material	% а	s supplied	as 100%
10	( 2) potassium hyd	roxide (50%)	12.00	6.00
	(3) ethanol		10.00	10.00
	( 4) palmitic acid		0.75	0.75
	( 5) oleic acid		5.50	5.50
	( 6) caprylic acid		1.50	1.50
15	(7) gluconic acid	Na-salt	0.50	0.50
	(8) alkane suphon	ic acid		
	Na-salt (30%)		1.50	0.30
	( 9) cumene sulphor	nic acid		
	Na-salt (40%)		14.00	4.00
20	(10) alkyl dimethy:	l benzyl		•
•	ammonium chlo	ride (50%)	3.00	1.50
	(11) ethylene diam	ine tetraacetic		
	acid 4 Na-sal	(40%)	10.00	4.00
	(12) sodium hydrox:	ide (50%)	4.00	2.00
25				
	( 1) water (deminer	calised) up to	100.00	100.0

# 30 Production method of composition 1

The raw materials were mixed together in the order given in brackets.

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Characteristics of composition 1

Appearance

: light yellow coloured clear

viscous liquid

5

Relative density (20°C) : 1.09

Viscosity :

Neat product

: 50-100 mPa.s at 21 s<sup>-1</sup> (Haake

10

MV1 25°C)

4% solution

: >120 mPa.s at 21  $s^{-1}$  (Haake MV1

25°C)

pH (1% solution)

: 12.3 - 12.5

15 Active alkalinity to

pH 8.2 (phenophtalein) : 4.2 - 4.6% as Na<sub>2</sub>O

Total alkalinity to

pH 3.6 (methyl orange) : 5.4 - 5.8% as Na<sub>2</sub>O

20

Composition 2: Heavy duty liquid detergent for foamgel and gel cleaning (low flash point).

5			
	Raw material %	as supplied	as 100%
	(2) potassium hydroxide (50%)	24.00	12.00
	(3) ethanol	10.00	10.00
	(4) palmitic acid	0.50	0.50
10	(5) oleic acid	5.25	5.25
	( 6) caprylic acid	1.50	1.50
	(7) gluconic acid Na-salt	0.50	0.50
	(8) alkane suphonic acid		
	Na-salt (30%)	1.50	0.45
15	( 9) cumene sulphonic acid		
	Na-salt (40%)	2.00	0.80
*	(10) alkyl dimethyl benzyl		
	ammonium chloride (50%)	2.25	1.13
	(11) ethylene diamine tetraaceti	С	•
20	acid 4 Na-salt (40%)	10.00	4.00
	(12) sodium hydroxide (50%)	6.00	3.00
			<u> </u>
	( 1) water (demineralised) to	100.00	100.0
25			
25			··

# Production method of composition 2

The raw materials were mixed together in the order given in brackets. The plant must be suitable for readily foamable products

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Characteristics of composition 2

Appearance : light yellow

: light yellow coloured clear

viscous liquid

5

Relative density (20°C) : 1.13

Viscosity :

Neat product : 50-100 mPa.s at 21 s<sup>-1</sup> (Haake

10 MV1 25°C)

4% solution : >120 mPa.s at 21 s<sup>-1</sup> (Haake MV1

25°C)

pH (1% solution) : 12.5 - 12.7

15 Active alkalinity to

pH 8.2 (phenophtalein) : 8.0 - 8.5% as Na<sub>2</sub>O

Total alkalinity to

pH 3.6 (methyl orange) : 9.2 - 9.6% as Na<sub>2</sub>O

20

5

Composition 3: Heavy duty liquid detergent for foamgel and gel cleaning of ovens and smoke chambers (low flash point).

	Raw material % a	s supplied	as 100%
	( 2) potassium hydroxide (50%)	32.50	16.25
	( 3) ethanol	10.00	10.00
10	( 4) palmitic acid	0.35	0.35
	( 5) oleic acid	5.50	5.50
	( 6) caprylic acid	2.75	2.75
	( 7) gluconic acid Na-salt	0.50	0.50
	(8) alkane suphonic acid		
15	Na-salt (30%)	1.50	0.45
•	( 9) cumene sulphonic acid		
	Na-salt (40%)	1.00	0.40
	(10) alkyl dimethyl benzyl		
	ammonium chloride (50%)	2.25	1.12
20	(11) ethylene diamine tetraacetic		
	acid 4 Na-salt (40%)	5.00	2.00
	(12) sodium hydroxide (50%)	7.00	3.50
			<del></del>
	( 1) water (demineralised) to	100.00	100.0
25			

# Production method of composition 3

The raw materials were mixed together in the order given in brackets. The plant must be suitable for readily foamable products.

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10

Characteristics of composition 3

Appearance

: light yellow coloured clear

viscous liquid

5

Relative density (20°C) : 1.15

10 Viscosity:

Neat product

: 50-100 mPa.s at  $21 \text{ s}^{-1}$  (Haake

MV1 25°C)

4% solution

: >120 mPa.s at 21  $s^{-1}$  (Haake MV1

25°C)

15 pH (1% solution) : 12.5 - 12.7

Active alkalinity to

pH 8.2 (phenophtalein) : 9.7 - 10.1% as Na<sub>2</sub>O

20 Total alkalinity to

pH 3.6 (methyl orange) : 10.7 - 11.1% as Na<sub>2</sub>O

### CLAIMS

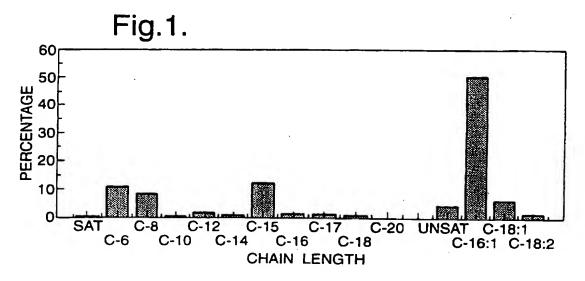
- 1. A cleaner concentrate composition which can be diluted to form a viscous use solution, the cleaner composition comprising:
- an ammonium compound and/or an amphoteric compound; and
   an anionic surfactant,
   wherein the composition is free of amine oxide.
- 2. A composition according to claim 1, which on dilution with water forms 1-20% by weight of a gel.
- 3. A composition according to claim 1 or 2, wherein the ammonium compound is a quaternary or a ternary ammonium compound.
- 4. Composition according to claim 3, wherein the ammonium compound is selected from the group consisting of benzalkonium chloride, primary, secondary or tertiary alkyl amines (C12-C27), and mixtures thereof.
- 5. Composition according to claim 3, comprising 1-25% by weight of the ammonium compound.
- 6. Composition according to claim 3, wherein the quaternary ammonium compound has a chain length of C8 C20, preferably C12 C16.
- 7. Composition according to claim 4, wherein the alkyl amine is tertiary for a pH of 9.5-10.0 and secondary for a pH of 3.5-4.0.
- 8. Composition according to any of the preceding claims, wherein the anionic surfactant consists of one or more

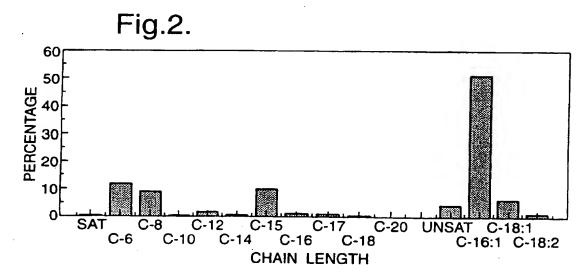
fatty acids neutralized by an alkaline source, these forming a soap.

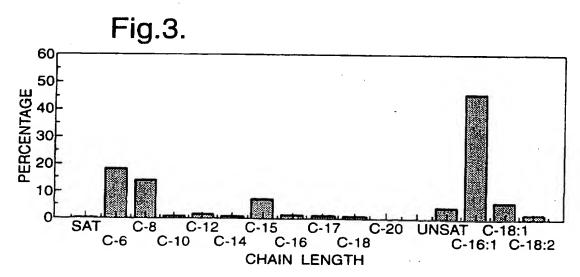
- 9. Composition according to claim 8, wherein the ratio of saturated to unsaturated fatty acids is 1:5, preferably 1:2.
- 10. Composition according to claim 8, wherein the fatty acids are selected from the group consisting of oleic acid, palmitic acid, caprylic acid, iso-stearic acid, and mixtures thereof.
- 11. Composition according to claim 8, wherein the alkaline source comprises 5-40% by weight of the composition.
- 12. Composition according to any of the preceding claims further comprising a cleaning agent selected from the group consisting of a secondary alkane sulphonate, an alkane sulphate, an ether sulphate, and mixtures thereof.
- 13. Composition according to claim 12, wherein the secondary alkane sulphonate is present at a concentration of 1 to 25% by weight of the composition.
- 14. Composition according to any of the preceding claims, further comprising a solvent selected from the group consisting of isopropanol, ethanol, hexylene glycol, propylene glycol, diethylene glycol, mono ethyl/butylether, dioxitol butyldioxitol, and mixtures thereof.
- 15. Composition according to any of the previous claims, having a flash point of between 25-50°C.
- 16. Composition according to any of the preceding claims, further comprising a sequestrant selected from the group consisting of ethylene-diamine-tetraacetic acid, nitrilo-

triacetic acid, citric acid, methylglycine-diacetic acid, serine diacetic acid, alkaline salts thereof, and mixtures thereof.

- 17. Composition according to claim 16, wherein the sequestrants are present at a level of from 0.1 to 15% by weight of the composition.
- 18. Cleaning method, comprising the steps of diluting a composition according to any of the preceding claims with water to a concentration to yield a desired viscosity and applying the composition thus diluted to a target surface.
- 19. A cleaning gel, obtainable by diluting the concentrate composition according to any of claims 1 17.
- 20. The use of a cleaning gel according to claim 19 for cleaning target surfaces.







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## INTERNATIONAL SEARCH REPORT

Inten al Application No PCT/EP 97/01176

A CLAS	SIFICATION OF SUBJECT MATTER		
IPC 6	C11D10/04 C11D1/65 C11D1	/94 C11D17/00	
According	to International Patent Classification (IPC) or to both national	classification and IPC	
	DS SEARCHED		
IPC 6	documentation searched (classification system followed by class C11D	ification symbols)	
Document	ation searched other than minimum documentation to the extent	that such documents are included in the fields	searched
Electronic	data base consulted during the international search (name of data	a base and, where practical, search terms used	)
C. DOCUM	MENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the	he relevant passages	Relevant to claim No.
х	WO 94 25561 A (NOVONORDISK AS E	T AL ) 10	
	November 1994 see claims 1-3,8-10	: AL.) 10	1,3,8, 10,11
A	CA 1 151 501 A (TASTAYRE GILLES August 1983	S M) 9	1
	see page 13, line 7 - line 8 see claims; examples		·
A	US 5 246 629 A (FUKUMOTO YOSHIN 21 September 1993 see the whole document	ORI ET AL)	1
	er documents are listed in the continuation of box C.	X Patent family members are listed in	n annex.
'A' documer	gories of cited documents :  It defining the general state of the art which is not  red to be of particular relevance	"T later document published after the inter- or priority date and not in conflict wit cited to understand the principle or the invention	h the application but
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citation	cited to establish the publication date of another or other special reason (as specified) at referring to an oral disclosure, use, exhibition or	"Y" document of particular relevance; the c cannot be considered to involve an inv	laimed invention
P" documen	eans t published prior to the international filing date but n the priority date claimed	ments, such combination being obvious in the art.	re other such docu- s to a person skilled
	tual completion of the international search	'&' document member of the same patent f  Date of mailing of the international sear	
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# INTERNATIONAL SEARCH REPORT

information on patent family members

Interr ial Application No
PCT/EP 97/01176

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9425561 A	10-11-94	AU 6720294 A CA 2162021 A EP 0697037 A JP 8509759 T NO 954401 A	21-11-94 10-11-94 21-02-96 15-10-96 03-11-95
CA 1151501 A	09-08-83	NONE	
US 5246629 A	21-09-93	JP 4085400 A	18-03-92

Form PCT/ISA-210 (patent family annex) (July 1992)